REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE	2. REPORT TYPE Professional Paper	3. DATES COVERED

4. TITLE AND SUBTITLE	
The Sense of Chromophore Orientation in Films Made by Alternating Polyelectrolyte Deposition	5a. CONTRACT NUMBER
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)	
Dr. Warren N. Herman	5d. PROJECT NUMBER
Dr. M. J. Roberts	5e. TASK NUMBER
	5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)	8. PERFORMING ORGANIZATION REPORT NUMBER
Naval Air Warfare Center Aircraft Division 22347 Cedar Point Road, Unit #6 Patuxent River, Maryland 20670-1161	

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR'S ACRONYM(S)
	11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

Alternating polyelectrolyte deposition (APD) is a technique for fabricating multilayer thin films at room temperature. The substrate is alternately dipped in two different aqueous solutions - one containing a polycation and the other a polyanion. By incorporating chromophores in the polycation and/or polyanion, it has been demonstrated that eh APD process can be used to make multilayer second order nonlinear optical polymer films. In additin, a recent encouraging discovery is that these films exhibit a high degree of thermal robustness.

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON Dr. Warren Herman and Dr. M. J. Roberts
a. REPORT	b. ABSTRACT	c. THIS PAGE			19b. TELEPHONE NUMBER (include area code)
Unclassified	Unclassified	Unclassified	SAR	12	(301) 342-9114 or (760)939-1394

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. Z39-18

20001031 064

THE SENSE OF CHROMOPHORE ORIENTATION IN FILMS MADE BY ALTERNATING POLYELECTROLYTE DEPOSITION**

W.N. Herman and M.J. Roberts*

Alternating polyelectrolyte deposition (APD) is a technique for fabricating multilayer thin films at room temperature.[1] The substrate is alternately dipped in two different aqueous solutions — one containing a polycation and the other a polyanion. By incorporating chromophores in the polycation and/or polyanion, it has been demonstrated that the APD process can be used to make multilayer second order nonlinear optical ($\chi^{(2)}$ NLO) polymer films.[2-8] In addition, a recent encouraging discovery is that these films exhibit a high degree of thermal robustness.[6-7]

The structure of the stilbazolium-substituted polyepichlorohydrin (SPECH) side-chain polymer used in fabricating $\chi^{(2)}$ NLO APD films is shown in Figure 1. Results of orientation measurements on two types of films are reported here: the first had SPECH layers alternated with poly(sodium 4-styrenesulfonate) (PSS) and the second had SPECH layers alternated with a weak polyanion - polyacrylic acid (PAA).

[*] Dr. W.N. Herman
U.S. Navy, NAWC Aircraft Division
EO Sensors Branch AIR4556
48110 Shaw Rd, Unit 5
Patuxent River, MD 20670

Dr. M.J. Roberts
U.S. Navy, NAWC Weapons Division
Chemistry and Materials Division AIR4T4220D
1 Administration Circle
China Lake, CA 93555

Determination of the orientation of the chromophores in an NLO film is essential to understanding and improving the fabrication process in a new technique such as APD. Estimates of the tilt angle are useful for assessing the degree of polar order obtained in a particular film, but knowing which end of the chromophore is up is crucial to understanding the details of the deposition process. From ratios of different second-harmonic d-coefficients, for example, it is possible to extract a tilt angle under the often-used assumption of a δ-function distribution.[9] The angle so obtained, however, is modulo 180° and as such does not determine "which end is up." The absolute sense of orientation can be determined from second-harmonic generation (SHG) phase measurements[10-12] using the setup depicted in Figure 2. The interference of the second harmonic (SH) generated by quartz with the SH generated by the sample can be varied using a glass plate as shown in the inset in Figure 2. Rotating the glass plate produces an intensity interferogram as a function of plate rotation angle. If the interferograms from two different films with similar chromophores are compared, they will be in phase if the absolute sense of orientation of the chromophores is the same (for example, acceptor ends of chromophores in both films are up) or be 180° out of phase if the absolute sense of orientation is opposite regardless of the tilt angle. The value of the tilt angle affects the relative magnitudes of SHG from the two films, but does not affect this phase issue. Effectively, the relative sign of $\chi^{(2)}$ with respect to a reference thin film is being measured and, for a chromophore with a 1-D charge transfer axis, $\chi^{(2)}$ is proportional to β_{zzz}, the dominant element of the hyperpolarizability,.

The interference data was least squares fit to the following expression for second-harmonic intensity describing the interference pattern as a function of the glass rotation angle θ:

$$I(\theta) = [E_q t_2(\theta)]^2 + [E_s t_1(\theta)]^2 + 2[E_q t_2(\theta)][E_s t_1(\theta)]\cos[\phi_q - \phi_s + \Delta\phi_2(\theta) - 2\Delta\phi_1(\theta)],$$

$$\Delta\phi_i = \frac{2\pi d}{\lambda_i}\left[\frac{n_i}{\cos(\theta_i)} + \left(1 + \frac{L}{d} - \frac{\cos(\theta - \theta_i)}{\cos(\theta_i)}\right)n_{ia}\right],$$

where $i = 1, 2$ for the fundamental and second-harmonic, respectively; n_i and n_{ia} are the refractive indices in glass and in air, respectively; $\sin(\theta_i) = \sin(\theta)/n_i$; $\lambda_2 = \lambda_1/2$; E_q and E_s are the amplitudes of the second-harmonic electric field generated by the quartz and sample, respectively; $t_1(\theta)$ and $t_2(\theta)$ are p-polarized Fresnel transmission coefficients for the glass, $d=1.248$mm is the thickness of the glass slide, and $L=210$mm is the separation distance between the sample and the quartz. The fitted parameters were E_q, E_s, and $\phi_0 = \phi_q - \phi_s$, where ϕ_q and ϕ_s are the initial phases of the SH at the surface of the quartz and sample, respectively. When comparing two different samples, the initial phase of the quartz cancels out and the relevant phase difference is $\delta\phi = \phi_s$(sample 2) $- \phi_s$(sample 1).

For the reference, we used a 20-bilayer AB accordion polymer Langmuir Blodgett Kuhn (LBK) film because the Langmuir Blodgett deposition process is well-established and MOPAC 7 simulations have been carried out for these polymers.[13] When this film was placed at the position marked "sample" in Figure 2, the interferograms that resulted are shown in Figure 3 indicated with solid-circle data points. The solid lines in the plots are least squares fits to the data to extract the phase ϕ_0 when the glass plate is perpendicular to the beam. The interferogram for a 53 bilayer SPECH/PSS film on a hydrophobic substrate is shown with open-circle data points in the top plot of Figure 3 and for a 51 bilayer SPECH/PAA film on base-washed glass with open-circle data points in the bottom plot of Figure 3. The SPECH/PSS interferogram is clearly in phase with the 20-bilayer AB LBK interferogram, while the SPECH/PAA

interferogram is out of phase with the 20-bilayer AB LBK interferogram. The least squares fits gave ~0° and ~180°, respectively, for the phase differences. Thus, as shown in Figure 4, the sense of orientation for the stilbazolium chromophore in the SPECH/PSS films deposited on hydrophobic glass is opposite to the sense of orientation of SPECH/PAA films deposited on hydrophilic glass are. The β-vectors shown in Figure 4 represent the irreducible vector part of the hyperpolarizability tensor. Data collected on an 83 bilayer SPECH/PSS film on a hydrophobic substrate and a 61 bilayer SPECH/PAA on base-washed glass gave the same results regarding the sense of orientation.

To determine whether the substrate hydrophobicity or the type of polyanion layer (PSS or PAA) was responsible for the difference in orientation, SPECH/PAA films were fabricated on hydrophobic glass. A direct comparison of the interferograms for a 51 bilayer SPECH/PAA film on base-washed glass with a 51 bilayer SPECH/PAA film on a hydrophobic substrate is shown in Fig. 5. The interferograms are clearly 180° out of phase indicating that the hydrophobicity of the substrate affects the sense of orientation.

Molecule-surface interactions with the first monolayer governing the orientation in thin films has been seen, as well, in other types of thin films.[14] For SPECH, the end of the chromophore with the pyridinium group near the backbone is relatively more hydrophilic than the opposite end of the chromophore. Our data indicates that this feature interacting with the hydrophobicity of the substrate is the dominant mechanism that determines the sense of orientation in the first layer and chromophores in subsequent layers adopt the same sense of orientation and the same order parameter of the previously deposited layers. It is well known that polyelectrolyte layers are interspersed[15] so it is not surprising that chromophores in the process of being deposited are influenced with previously deposited layers. These results demonstrate that the chromophore

orientation in the first layer 'directs' the chromophore orientation throughout the $\chi^{(2)}$ NLO APD films and suggests new strategies for improvement of polar order in these films. Experiments are underway to test this hypothesis. The practical implications of these results include the possibility to pattern a substrate with hydrophobic and hydrophilic regions to control the sense of chromophore orientation in each region. This might be done to produce a push-pull Mach-Zehnder interferometer, for example.

Experimental

The $\chi^{(2)}$ NLO APD films were fabricated at room temperature in ambient air using a computer-interfaced Zeiss HMS Programmable Slide Stainer that was kept in a Class 100 clean room under UV/blue blocked fluorescent light. The SPECH/PSS films were deposited on hydrophobicized glass slides and the SPECH/PAA films on both hydrophobic and base-washed glass slides. The 1319nm line of a diode-pumped Nd:YAG laser was used as the fundamental for the SHG measurements.

[1] J. H. Cheung, A. F. Fou, M. F. Rubner, *Thin Solid Films* **1994**, *224*, 985.

[2] Y. Lvov, S. Yamada, and T. Kunitake, *Thin Solid Films* **1997**, *300*, 107.

[3] X. Wang, S. Balasubramanian, L. Li, X. Jiang, D.J. Sandman, M.F. Rubner, J. Kumar, S.K. Tripathy, *Macromol. Rapid Commun.* **1997**, *18*, 451.

[4] K. M. Lenahan, Y. Wang, Y. Liu, R. O. Claus, J. R. Heflin, D. Marciu, C. Figura, *Adv. Mater.* **1998**, *10(11)*, 853.

[5] M. J. Roberts, in Organic Nonlinear Optical Materials and Devices (Eds. B. Kippelin, H. Lackritz, R. Claus), *Proc. of Mat. Res. Soc.* **1999**, *561*, 33.

[6] M. J. Roberts, G. A. Lindsay, W. N. Herman, K. J. Wynne, *J. Am. Chem. Soc.* **1998**, *120*, 11202.

[7] J.R. Heflin, C. Figura, D. Marciu, Y. Liu, R.O. Claus, *Appl. Phys. Lett.* **1999**, *74*, 495.

[8] M. J. Roberts and W. N. Herman, in Electrical, Optical, and Magnetic Properties of Organic Solid-State Materials V (Eds. S.P. Ermer, J.R. Reynolds, J.W. Perry, A.K-Y. Jen, Z. Bao), *Proc. of Mat. Res. Soc.* **1999**, *598*, BB4.3.

[9] A method for determining a more general orientational distribution function is given by B. Park, Y. Kinoshita, and H. Takezoe, *Phys. Rev.* **1998**, *E57*, 6717.

[10] X. Liu, L. Liu, and X. Lu, *Thin Solid Films* **1992**, *217*, 174.

[11] K. Kajikawa, H. Takezoe, and A. Fukuda, *Langmuir* **1996**, *12*, 580.

[12] H. Kimura-Suda, T. Wada, W. Liang, H. Nakahara, and H. Sasabe, *Proc. SPIE* **1998**, *3474*, 68.

[13] G. Lindsay, K. Wynne, W. Herman, A. Chafin, R. Hollins, J. Stenger-Smith, J. Hoover, J. Cline, and J. Roberts, *Nonlinear Optics* B **1996**, *15*, 139.

[14] T. Kikteva, D. Star, and G.W. Leach, *J. Phys. Chem. B* **2000**, *104*, 2860.

[15] G. Decher, *Science* **1997**, *277*, 1232.

Figure Captions

Figure 1.   Structure of the SPECH polycation.

Figure 2.   Arrangement for making SHG interference measurements. Inset: The glass slide is rotated from $\theta = -90°$ to $+90°$ to vary the phase difference between the SHG from quartz and from the sample, which then interfere to produce an intensity modulation.

Figure 3.   Superposition of SHG interferograms for 20-bilayer AB accordion polymer LBK film (solid circles, top and bottom plots) with 53-bilayer SPECH/PSS APD film on a hydrophobic substrate(open circles, top plot) and 51-bilayer SPECH/PAA on a base-washed substrate(open circles, bottom plot). The solid lines are least squares fits to the data.

Figure 4.   Orientations of the stilbazolium chromophore in APD films on (b) HMDS treated glass and (c) base-washed glass as deduced from comparison of interferograms with the reference (a) AB accordion polymer LBK film.

Figure 5.   Superposition of SHG interferograms for a 51-bilayer SPECH/PAA film on a hydrophobic substrate (open circles) and a 51-bilayer SPECH/PAA film on a base-washed substrate (solid circles) indicating opposite senses of chromophore orientation in the two films.
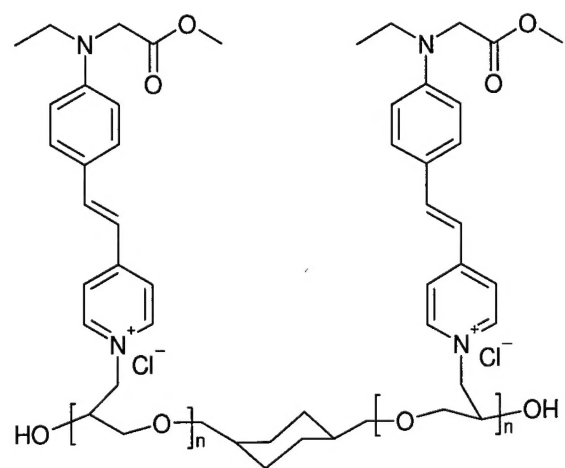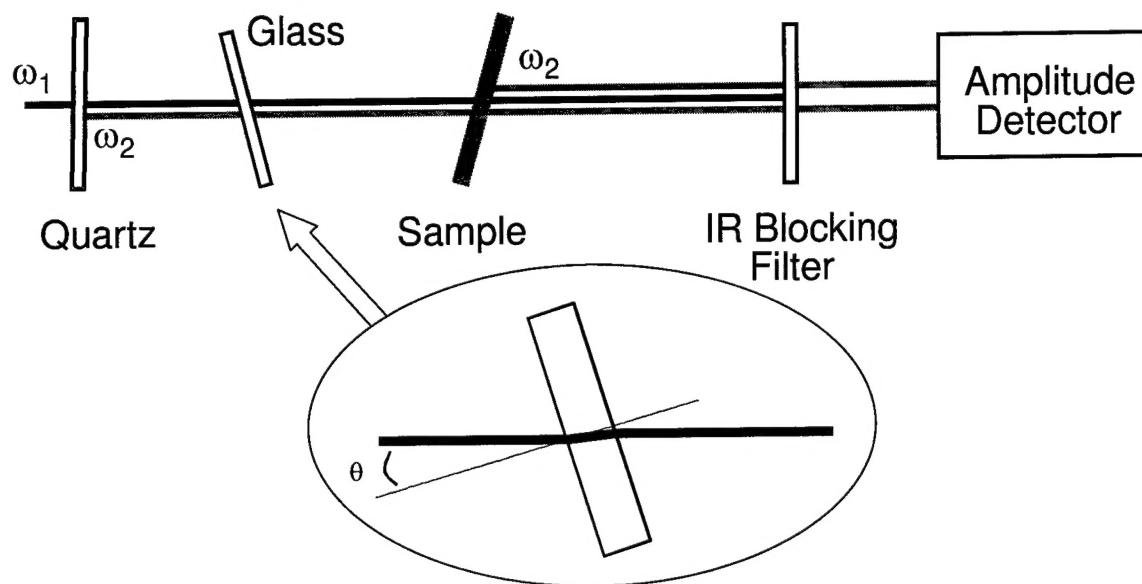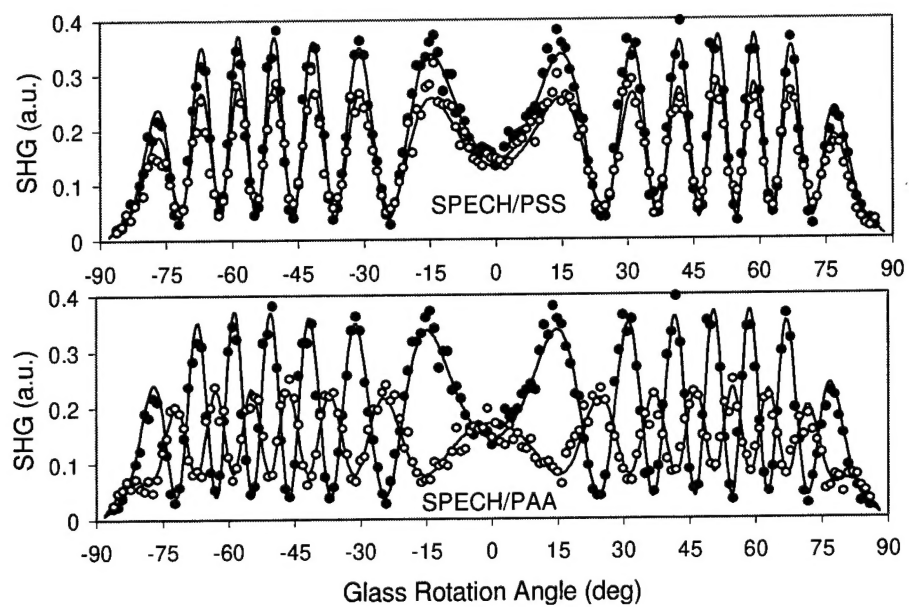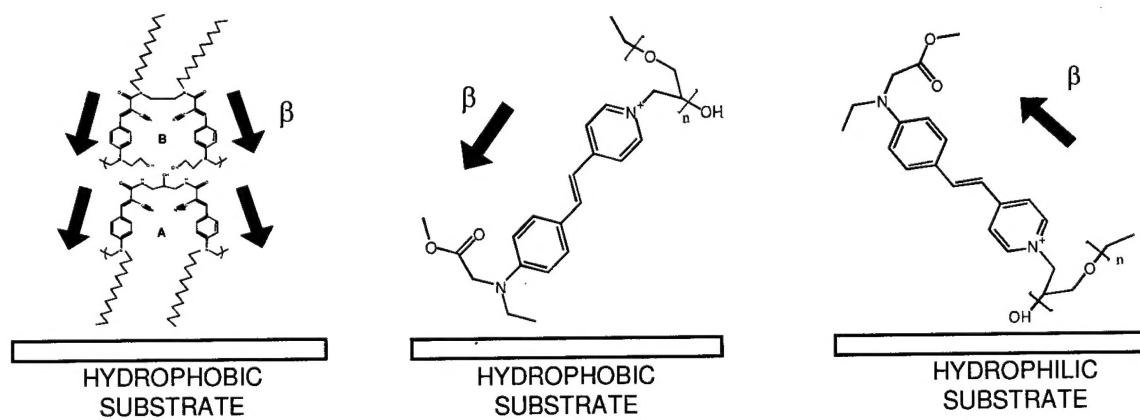
Figure 1.

ω₁
ω₂
Glass
Quartz
ω₂
Sample
IR Blocking
Filter
Amplitude
Detector
θ

Figure 2.

Figure 3.

HYDROPHOBIC
SUBSTRATE

HYDROPHOBIC
SUBSTRATE

HYDROPHILIC
SUBSTRATE

Figure 4

Figure 5.